diffusion-fundamentals
The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

Diffusional Atomic-Ordering Kinetics of Close-Packed Solid Solutions: Models for $L1_2$ and $D0_{19}$ Phases

Taras Radchenko[1], *Valentyn Tatarenko*[1], *Hélèna Zapolsky*[2]

[1] Department of Solid State Theory, Institute for Metal Physics, N.A.S. of Ukraine, 36 Vernadsky Blvd., 03680 Kyiv-142, Ukraine, E-Mail: Taras.Radchenko@gmail.com
[2] Institut des Materiaux, UFR Sciences et Techniques, Université de Rouen, Avenue de l'Université—B.P. 12, 76801 Saint-Etienne du Rouvray, France

1. Introduction

Ordering in solid solutions is a topic of growing technological and scientific interest within the field of material science. This is because of the advantageous high temperature and corrosion properties of alloys which are linked to the effect of long-range ordering [1]. Long-range order kinetics is one of the diffusion processes occurring within the atomic ranges. X-ray diffraction technique is the most convenient experimental instrument to provide us detailed information on this process. There are also different theoretical methods for this one. One of the models is based on the Onsager-type microscopic-diffusion equation [1].

2. Kinetics model

To investigate the kinetics of the diffusional ordering process in close-packed, i.e. face-centered cubic or hexagonal close-packed, lattices, we take a model based on the Onsager-type microscopic-diffusion equation [1]. For the exchange substitutional diffusion mechanism in $A_{1-c}B_c$ solid solution, the single-site occupation-probability function, $P(\mathbf{R},t)$, is proportional to the thermodynamic driving force, $\delta F/\delta P(\mathbf{R}',t)$:

$$\frac{dP(\mathbf{R},t)}{dt} \propto -\sum_{\mathbf{R}'} L(\mathbf{R}-\mathbf{R}')\frac{\delta F}{\delta P(\mathbf{R}',t)}.$$

Here, t is a time, $L(\mathbf{R}-\mathbf{R}')$ is the kinetic coefficient representing the exchange probability of an elementary diffusional jump between a pair of atoms from site $\mathbf{R}$ of to $\mathbf{R}'$, and vice versa, during the time unit, F is a configurational free energy.

Using the above-mentioned equation, the self-consistent field (mean-field) approximation along with the static concentration waves' approach, an equation for the time dependence of long-range order parameter, η, in the $L1_2$ and $D0_{19}$ types structures is as follows:

$$\frac{d\eta}{dt} = -\tilde{L}(\mathbf{k})\left(\frac{\eta}{T^*} + \ln\frac{(c_B+3\eta/4)(1-c_B+\eta/4)}{(1-c_B-3\eta/4)(c_B-\eta/4)}\right),$$

where T^* is a reduced temperature, $\tilde{L}(\mathbf{k})$ is the Fourier transform of the Onsager-type kinetic coefficients, and $\mathbf{k}$ is a superlattice wave vector generating the $L1_2$ or $D0_{19}$ types superstructures, c_B is an atomic fraction of B atoms.

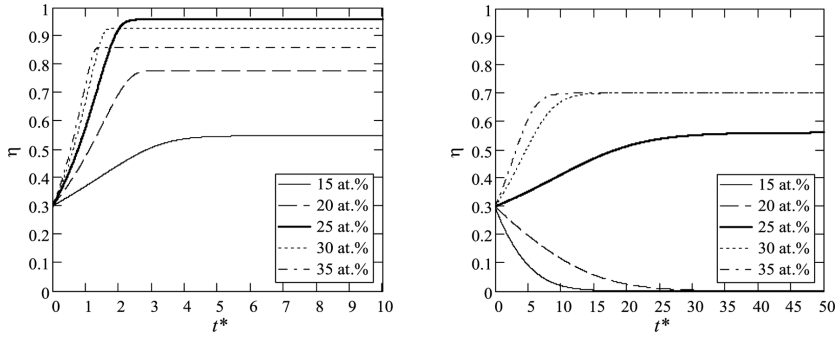

Fig. 1: The reduced-time dependences of $L1_2$- and $D0_{19}$-type LRO parameters for different atomic fractions of alloying component at the reduced temperatures $T^* = 0.12$ (left) and $T^* = 0.20$ (right).

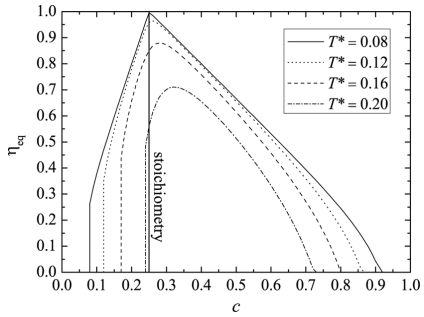

Fig. 2: Equilibrium long-range order parameter vs. atomic fraction of alloying component for $L1_2$ and $D0_{19}$ types phases at different reduced temperatures.

3. Results and conclusions

The last equation permitted obtaining the time dependence of LRO for a wide temperature–concentration range (Fig. 1). The curves (showing the order-parameter relaxation kinetics) are also obtained for both temperature-independent interaction parameters and temperature-dependent ones. The kinetics results confirm the statistical-thermodynamics ones (Fig. 2). Firstly, equilibrium LRO parameters, η_{eq}, coincide within the frameworks of both models. Secondly, for the non-stoichiometric alloys (where an atomic fraction of alloying component B is more than $c_B^{st} = 0.25$), the equilibrium LRO parameter can be higher than it is for stoichiometric ones at high temperatures (Figs. 1 and 2). The experimental phase diagrams confirm the predicted (ordered or disordered) states for close-packed f.c.c. Ni–Fe and h.c.p. Ti–Al alloys.

References

[1] A.G. Khachaturyan, Theory of Structural Transformations in Solids, John Wiley & Sons, New York, 1983.